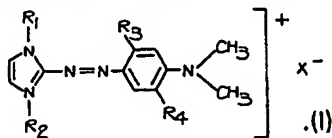


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- (71) Applicant
Bayer Aktiengesellschaft,
509 Leverkusen-
Bayerwerk, Germany
- (72) Inventor
Hans-Peter Kühlthau
- (74) Agent
Carpmaels & Ransford

(54) Cationic Dyestuffs

(57) Cationic dyestuffs of the formula



wherein

R₁ and R₂ independently of one

another represent a lower alkyl,
alkenyl or hydroxyalkyl radical,

R₃ represents a lower alkyl, alkenyl
or alkoxy radical,

R₄ represents H, halogen or a lower
alkyl, alkenyl or alkoxy radical and

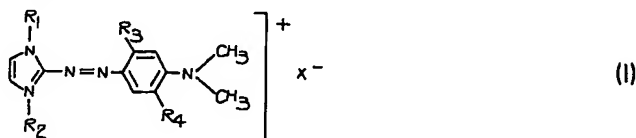
X⁻ represents an anion,
are used for dyeing and printing
natural and synthetic materials, in
particular polyacrylonitrile.

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SPECIFICATION

Cationic Dyestuffs

The invention relates to new cationic dyestuffs of the general formula



5 wherein

R_1 and R_2 independently of one another represents a lower alkyl, alkenyl or hydroxyalkyl radical,
 R_3 represents a lower alkyl, alkenyl or alkoxy radical,
 R_4 represents H, halogen, or a lower alkyl, alkenyl or alkoxy radical and
 X^- represents an anion,

10 their preparation and their use for dyeing and printing natural and synthetic materials.

By lower alkyl and alkoxy groups there are understood, in particular, straight-chain or branched radicals with 1 to 4 C atoms. Lower alkenyl radicals are, in particular, those with 3 or 4 C atoms, above all the allyl, butenyl and i-butenyl radical. Halogen represents, above all, fluorine and chlorine.

The anion X^- can be derived from inorganic and organic acids. Examples of inorganic anions and
 15 fluoride, chloride, bromide and iodide, perchlorate, hydroxyl, radicals of acids containing S, such as
 bisulphate, sulphate, disulphate and aminosulphate; radicals of nitrogen-oxygen acids, such as nitrate;
 radicals of oxygen acids of phosphorus, such as dihydrogen phosphate, hydrogen phosphate,
 phosphate and metaphosphate; radicals of carbonic acid, such as bicarbonate and carbonate; further
 anions of oxygen acids and complex acids, such as methosulphate, ethosulphate, hexafluorosilicate,
 20 cyanate, thiocyanate, trichlorozincate and tetrachlorozincate, tribromozincate and tetrabromozincate,
 borate and tetrafluoroborate, as well as anions of esters of boric acid, such as of the glycerol ester of
 boric acid, and of esters of phosphoric acid, such as of methylphosphate.

Examples of organic anions are anions of saturated or unsaturated aliphatic, cycloaliphatic,
 aromatic and heterocyclic carboxylic acids and sulphonic acids, such as radicals of formic acid, acetic
 25 acid, chloroacetic acid, cyanoacetic acid, hydroxyacetic acid, aminoacetic acid, methylaminoacetic acid,
 aminoethylsulphonic acid, methylaminoethylsulphonic acid, propionic acid, n-butyric acid, i-butyric
 acid, 2-methyl-butyric acid, 2-ethyl-butyric acid, dichloroacetic acid, trichloroacetic acid, trifluoroacetic
 acid, 2-chloropropionic acid, 3-chloropropionic acid, 2-chlorobutyric acid, 2-hydroxypropionic acid, 3-
 hydroxypropionic acid, O-ethylglycollic acid, thioglycollic acid, glyceric acid, malic acid, dodecyl-
 30 tetraethylene glycol ether-propionic acid, phenoxyacetic acid, nonylphenoxyacetic acid, n-valeric acid,
 i-valeric acid, 2,2,2-trimethylacetic acid, n-caproic acid, 2-ethyl-n-caproic acid, stearic acid, oleic acid,
 ricinoleic acid, palmitic acid, n-pelargonic acid, lauric acid, a mixture of aliphatic carboxylic acids with
 9—11 carbon atoms (Versatic Acid 911 from Shell), acrylic acid, methacrylic acid, crotonic acid,
 propargylic acid, oxalic acid, malonic acid, succinic acid, adipic acid, pimelic acid, suberic acid, the
 35 isomer mixture of 2,2,4- and 2,4,4-trimethyladipic acid, sebacic acid, isosebacic acid (isomer mixture),
 tartaric acid, citric acid and glyoxylic acid.

Examples of suitable anions of cycloaliphatic carboxylic acids are the anions of
 cyclohexanecarboxylic acid and cyclohexene-3-carboxylic acid and examples of anions of araliphatic
 monocarboxylic acids are anions of phenylacetic acid, 4-methylphenylacetic acid and mandelic acid.

40 Examples of suitable anions of aromatic carboxylic acids are the anions of substituted and
 unsubstituted benzoic acid and of phthalic acid, tetrachlorophthalic acid, 4-hydroxyphthalic acid, 4-
 methoxyphthalic acid, isophthalic acid, 4-chloro-iso-phthalic acid, 5-nitro-iso-phthalic acid,
 terephthalic acid, nitroterephthalic acid and diphenyl-3,4-carboxylic acid, o-vanillic acid, 3-
 sulphobenzoic acid, benzene-1,2,4,5-tetracarboxylic acid, naphthalene-1,4,5,8-tetracarboxylic acid,
 45 biphenyl-4-carboxylic acid, abietic acid, phthalic acid mono-n-butyl ester, terephthalic acid mono-
 methyl ester, 3-hydroxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid, 2-hydroxy-1-naphthoic acid
 and anthraquinone-2-carboxylic acid.

Examples of suitable anions of aromatic sulphonic acids are the anions of benzenesulphonic acid,
 benzene-1,3-disulphonic acid, 4-chlorobenzenesulphonic acid, 3-nitrobenzenesulphonic acid, 6-
 50 chloro-3-nitrobenzenesulphonic acid, toluene-4-sulphonic acid, toluene-2-sulphonic acid, toluene- ω -
 sulphonic acid, 2-chlorotoluene-4-sulphonic acid, 2-hydroxybenzenesulphonic acid and n-
 dodecylbenzenesulphonic acid.

Colourless anions are preferred. For dyeing from an aqueous medium, anions which do not
 excessively impair the solubility of the dyestuff in water are preferred. For dyeing from organic solvents,
 55 anions which assist the solubility of the dyestuff in organic solvents or at least do not influence it
 adversely are frequently also preferred.

The anion is in general decided by the preparation process and by the purification of the crude
 dyestuff which may be carried out. In general, the dyestuffs are in the form of zinc chloride double salts,

acetates, methosulphates, ethosulphates or halides (in particular as chlorides or bromides). The anions can be replaced by other anions in a known manner.

In preferred dyestuffs of the formula I,

R_1 and R_2 represents methyl or ethyl,

5 R_3 represents methyl, ethyl, methoxy or ethoxy,

R_4 represents H, fluorine, chlorine, methyl, ethyl, methoxy or ethoxy and

X^- represents an anion.

Of these dyestuffs, those examples in which

R_1 and R_2 represent methyl,

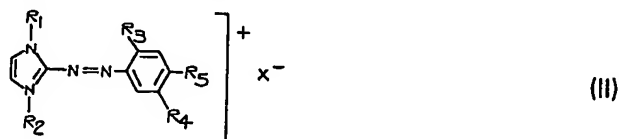
10 R_3 represents methyl or methoxy and

R_4 represents H,

are particularly interesting.

The new dyestuffs of the general formula I are obtainable by known processes, such as are described, for example, in German Patent Specifications 1,098,642, 1,137,815 and 1,137,816.

15 The dyestuffs are obtained, for example, by reacting compounds of the formula



with dimethylamine.

In formula II,

R_1 , R_2 , R_3 and R_4 have the meanings given in the case of formula I.

20 R_5 denotes a group which can be split off by dimethylamine, for example an alkoxy group, an alkylthio group or a halogen atom.

R_5 can also denote hydrogen. The reaction with dimethylamine is then carried out in the presence of an oxidizing agent, such as, for example, atmospheric oxygen.

25 The reactions of II with dimethylamine can be carried out in aqueous solution or suspension, in the presence of organic solvents or mixtures thereof with water, at room temperature or elevated temperature. Many of the compounds already react between 0° and 20°C.

Compounds of the formula II are prepared in a known manner by diazotising aminobenzenes of the formula



30 wherein

R_3 , R_4 and R_5 have the meanings given in the case of formula II, coupling the diazotisation product to imidazole and then reacting the resulting compounds

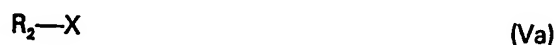


wherein

35 R_3 , R_4 and R_5 have the meaning given in the case of formula II, with compounds having an alkylating action, of the formula

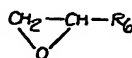


or



40 wherein

R_1 and R_2 have the meaning given in the case of formula I, and X is a group which supplies an anion X^- , or with oxiranes of the formula



wherein

45 R_6 represents H, methyl or ethyl.

Examples of suitable diazo components (III) are; 2-methoxy-4-chloroaniline; 2-methyl-4-chloroaniline; o-anisidine; o-toluidine; 2,4-dimethoxyaniline; 2-methyl-4-methoxyaniline; 2-methyl-5-chloroaniline; 2-ethylaniline; 2,5-dimethylaniline; o-phenetidine; 2-methoxy-5-chloroaniline; 2-methoxy-4,5-dichloroaniline; 2-methyl-5-methoxyaniline; 2-methoxy-5-methylaniline; 2-ethoxy-5-

methylaniline; 2-methoxy-4-chloro-5-methylaniline; 2-propoxy-5-methylaniline; 2,4-dimethoxy-5-chloroaniline; 2,5-dimethoxyaniline; 2,5-dimethoxy-4-chloroaniline; 2,5-diethoxyaniline; 2-isopropylaniline; 4-fluoro-2-methylaniline; and 5-fluoro-2-methylaniline.

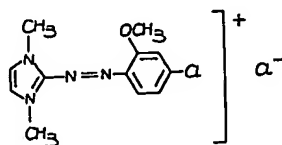
The new dyestuffs are suitable for dyeing, printing and bulk dyeing materials containing acid groups, above all products which consist completely or predominantly of polymerised unsaturated nitriles, such as acrylonitrile and vinylidene dicyanide, or of acid-modified polyamides or polyesters. They are furthermore suitable for the other known applications of cationic dyestuffs, such as dyeing and printing cellulose acetate, coir, jute, sisal and silk and of tannin-treated cotton and paper, and for the preparation of ball-point pen pastes and rubber-stamp inks and for use in transfer printing and in flexographic printing. The dyeings and prints on the materials first mentioned, in particular on polyacrylonitrile, are distinguished by their very high level of fastness, above all by very good fastness to light, wet processing, rubbing, decatising, sublimation and perspiration.

The new dyestuffs furthermore have a very good levelling power, which enables uniform dyeings to be achieved on acrylonitrile fibres, even in light shades, without greater dyeing technology requirements and without the addition of a retarder.

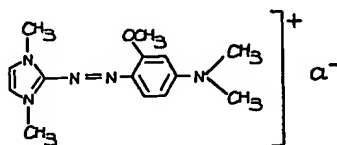
The new dyestuffs also have a good affinity and can readily be combined both with other dyestuffs which migrate well and with dyestuffs with not such a good levelling power.

Example 1

30 g of the dyestuff of the formula

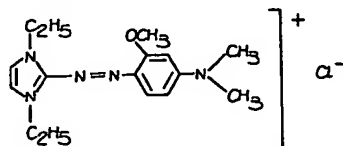


obtained by coupling diazotised 2-methoxy-4-chloroaniline to imidazole, subsequent methylation with dimethyl sulphate, solution in water and precipitation with NaCl, are stirred in a mixture of 31 g of concentrated hydrochloric acid and 25 g of a 46% strength dimethylamine solution. A further few ml of the dimethylamine solution are then added dropwise at 90°C until the reaction is complete, which can easily be established by a thin layer chromatogram. The mixture is then cooled and diluted with 100 ml of saturated sodium chloride solution and the pH value is adjusted to 5 with hydrochloric acid. The resulting dyestuff of the formula



is filtered off. It dyes polyacrylonitrile yellowish-tinged red with good fastness properties and a good levelling power.

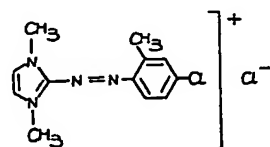
If diethyl sulphate is used in the preparation of the starting dyestuff instead of dimethyl sulphate and the further procedure following is then as indicated above, the dyestuff of the formula



is obtained. It dyes polyacrylonitrile with a fast red colour shade.

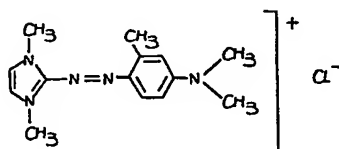
35 Example 2

20 g of the dyestuff of the formula

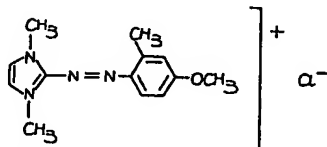


obtained by coupling diazotised 2-methyl-4-chloroaniline to imidazole, subsequent methylation with dimethyl sulphate, solution in water and precipitation with NaCl, are reacted with dimethylamine analogously to Example 1. The resulting dyestuff dyes polyacrylonitrile in a bluish-tinged red with good fastness properties.

It has the formula

**Example 3**

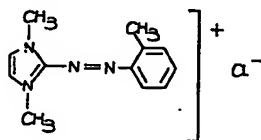
20 g of the dyestuff of the formula



- 5 obtained by coupling diazotised 2-methyl-4-methoxyaniline to imidazole, subsequent methylation with dimethyl sulphate, solution in water and precipitation with NaCl, are reacted with dimethylamine as described in Examples 1 and 2. The resulting dyestuff is identical to the product prepared according to Example 2. 5

Example 4

20 g of the dyestuff of the formula



- obtained by coupling diazotised o-toluidine to imidazole, subsequent methylation with dimethyl sulphate, solution in water and precipitation with NaCl, are stirred with 35 ml of a 46% strength dimethylamine solution at room temperature in the presence of atmospheric oxygen until no further starting dyestuff can be detected in a thin layer chromatogram. 15
- The mixture is then diluted with 100 ml of saturated sodium chloride solution and the pH value is adjusted to 5 with hydrochloric acid.
- The resulting dyestuff is filtered off. It is identical to the product described in Example 2.
- The dyestuffs of the general formula 15



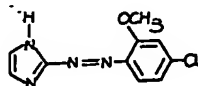
are obtained by the processes indicated in Examples 1, 3 and 4.

The table which follows contains some further examples prepared, the colour shade on polyacrylonitrile being indicated

25	Example No.	R_3	R_4	Colour shade on polyacrylonitrile	25
	5	OCH_3	CH_3	bluish-tinged red	
	6	"	OCH_3	blue-red	
	7	"	Cl	bluish-tinged red	
	8	CH_3	CH_3	claret	
30	9	$\text{CH}(\text{CH}_3)_2$	H	red	30
	10	CH_3	F	red	
	11	C_2H_5	H	bluish-tinged red	
	12	OC_2H_5	H	red	

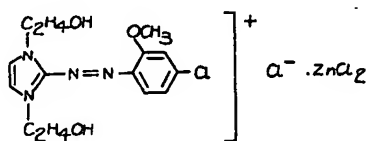
Example 13

35 20 g of the azo dyestuff of the formula



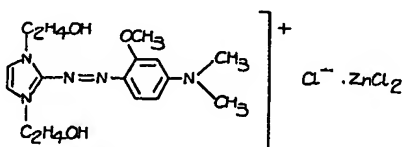
prepared by coupling diazotised 2-methoxy-4-chloroaniline to imidazole are stirred in 30 ml of glacial acetic acid. Ethylene oxide is then passed in at 50°C until the reaction, which can easily be followed by

a thin layer chromatogram, has ended. The mixture is then diluted with 500 ml of saturated sodium chloride solution and the dyestuff of the formula



is precipitated with zinc chloride.

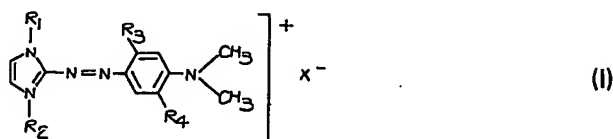
- 5 If this dyestuff is reacted with dimethylamine by a process analogous to that described in Example 1, the dyestuff of the formula



is obtained. It dyes polyacrylonitrile red.

Claims

- 10 1. A dyestuff of the general formula



in which R₁ and R₂ independently of each other denote a C₁ to C₄ alkyl, C₃ or C₄ alkenyl or hydroxyalkyl group,

R₃ denotes a C₁ to C₄ alkyl, C₃ or C₄ alkenyl or C₁ to C₄ alkoxy group,

- 15 R₄ denotes a hydrogen or halogen atom or a C₁ to C₄ alkyl, C₃ or C₄ alkenyl or C₁ to C₄ alkoxy group and

X⁻ denotes an anion.

2. A dyestuff according to Claim 1, in which

R₁ and R₂ independently of each other denote a methyl or ethyl group,

- 20 R₃ denotes a methyl, ethyl, methoxy or ethoxy group and

R₄ denotes a hydrogen, fluorine or chlorine atom or a methyl, ethyl, methoxy or ethoxy group.

3. A dyestuff according to Claim 2, in which

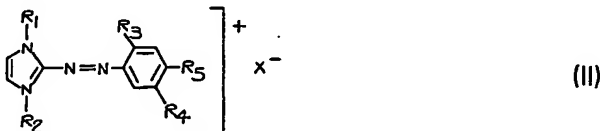
R₁ and R₂ denote methyl groups,

R₃ denotes a methyl or methoxy group and

- 25 R₄ denotes a hydrogen atom.

4. A dyestuff according to Claim 1 as hereinbefore specifically identified.

5. A process for the production of a dyestuff as claimed in Claim 1, in which a compound of the general formula



- 30 in which

R₁, R₂, R₃, R₄ and X⁻ have the same meanings as in Claim 1, and

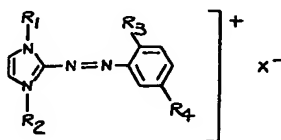
R₅ denotes a group which can be split off by dimethylamine, is reacted with dimethylamine.

6. A process according to Claim 5, in which R₅ denotes an alkoxy group, an alkylthio group or a halogen atom.

- 35 7. A process according to Claim 5 or 6, in which the reaction is carried out in aqueous solution or suspension, in the presence of an organic solvent or a mixture thereof with water, at a temperature between 0° and 120°C.

8. A process according to Claim 7 in which the reaction is carried out at a temperature between 20 and 90°C.

- 40 9. A process for the production of a dyestuff as claimed in Claim 1, in which a compound of the general formula



In which R_1 , R_2 , R_3 , R_4 and X^- have the same meanings as in Claim 1, is reacted with dimethylamine in the presence of an oxidising agent.

10. A process according to Claim 9, in which the reaction is carried out in aqueous solution or suspension, in the presence of an organic solvent or a mixture thereof with water, at a temperature between 0° and 120°C. 5
11. A process according to Claim 10 in which the reaction is carried out at a temperature between 20 and 90°C.
12. A process according to any of Claims 9 to 11, in which the oxidising agent is atmospheric oxygen.
- 10 13. A process for the production of a dyestuff as claimed in Claim 1 when carried out substantially as described in any one of the examples. 10
14. A dyestuff according to Claim 1 when produced by the process of any of Claims 5 to 13.
15. A process for dyeing or printing a textile material of polyacrylonitrile, of an acid modified polyester or of an acid-modified polyamide, comprising treating the textile material with a dyestuff as claimed in any of Claims 1 to 4 and 14. 15
16. A process for dyeing or printing a material which is cellulose acetate, coir, jute, sisal, silk, tannin-treated cotton or paper or for colouring a material which is a ball-point pen paste, a rubber-stamp ink, a transfer printing ink or a flexographic printing paste comprising treating the material with or incorporating therein a dyestuff as claimed in any of Claims 1 to 4 and 14.
- 20 17. A textile material of polyacrylonitrile, of an acid modified polyester or of an acid-modified polyamide when dyed or printed by the process as claimed in Claim 15. 20
18. A material as defined in Claim 16 when dyed, printed or coloured by the process of Claim 16.